DIAS-STP-84-51

THE STOCHASTIC MECHANICS OF THE GROUND-STATE OF THE HYDROGEN ATOM

A. Truman
Department of Mathematics
University College of Swansea
Singleton Park, Swansea SA2 8PP
Wales

J.T. Lewis
Dublin Institute for Advanced Studies
10 Burlington Road, Dublin 4
Ireland

Talk given by A. Truman at the BiBoS - Symposium

Bielefeld, September, 1984.

1. Introduction

The prospect of a formulation of quantum mechanics on path space, ffered by Nelson's stochastic mechanics, is attractive to many. So ar, it has been shown to be in complete agreement with the Schrödinger heory at the level of particle densities and spectra. But stochastic echanics, because it operates at the sample-path level, seems to contain ore information than the Schrödinger theory. The sample-paths in tochastic mechanics satisfy Nelson's generalization of Newton's equation see §3 below); it is tempting, therefore, to conjecture that the ample-paths of the process provide us with the ensemble of actual article paths. In this paper we explore one consequence of this onjecture.

If the Nelson theory is to be more than a very elegant reformulation f Schrödinger's wave-mechanics, one must find areas where the predictions f stochastic mechanics and quantum theory differ. One area which merits nvestigation is the calculation of first hitting times in stochastic echanics and first detection times in quantum theory. As a first step n this direction we consider the stochastic mechanics of the stationary tates of the Hydrogen atom, a readily identifiable quantum system.

In this paper we analyze in detail the diffusion process corresponding o the ground state of the Hydrogen atom; we obtain a skew-product ormula for the process and give detailed results on first-hitting times. n [1] we describe how first arrival times of quantum particles can be alculated in the quantum theory of counting processes due to Davies [2]. inally, we indicate how our results may be extended to excited states.

Since this is addressed to a mixed audience of physicists and mathematicians, we have concentrated on explaining the ideas. The proofs are given in outline; details will be given in [1].

It is a pleasure to thank David Williams and Barry Simon for helpful conversations and to acknowledge SERC support through research grant GR/C/13644.

§2. Diffusion Processes and Schrödinger's Equation

First we recall some results about diffusion processes (see [3] for details). Let X be a process on $\mathbb{R}^d$ satisfying the Itô equation

$$dX_t = b(X_t,t)dt + dB_t \tag{2.1}$$

where B is a BM($\mathbb{R}^d$), a Brownian motion on $\mathbb{R}^d$, so that each component B^j of B is a Gaussian process with $E[B^j]=0$ and

$$E[B^j_s B^k_t] = \delta_{jk} \cdot s \text{ t, } i,j = 1,\ldots,d. \tag{2.2}$$

Here E [.] denotes the expectation with respect to Wiener measure P. If the drift b is sufficiently well-behaved, the process X has a transition density p(x,s ; y,t), defined for t>s by

$$P[X_t \in A, X_s = x] = \int_A p(x,s\,;y,t)dy, \tag{2.3}$$

and p is the fundamental solution of the forward Kolmogorov equation

$$\frac{\partial p}{\partial t} = \operatorname{div}_y (\tfrac{1}{2}\operatorname{grad}_y p - b(y,t)p) \overset{\text{def}}{=} L_y p, \tag{2.4}$$

subject to the condition

$$p(x,t\,;y,t) = \delta(x-y). \tag{2.5}$$

The subscript y on the differential operators indicates that differentiation is with respect to the final point y. Regarded as a function of the starting point x, the transition density p satisfies

$$\frac{\partial p}{\partial t} = \tfrac{1}{2}\Delta_x p + b(x,t)\operatorname{grad}_x p \overset{\text{def}}{=} L^* p, \tag{2.6}$$

the backward Kolmogorov equation. Here L^* is the formal L^2 - adjoint of L.

Now let f(x,t) be a classical solution of the Schrödinger equation

$$i\frac{\partial f}{\partial t} = -\tfrac{1}{2}\Delta_x f + Vf, \tag{2.7}$$

where V is a real-valued potential function. Multiplying by f*, the complex conjugate of f, and equating real parts, we find that the continuity equation

$$\frac{\partial \rho}{\partial t} + \operatorname{div} j = 0 \tag{2.8}$$

is satisfied by the quantum mechanical probability density $\rho = |f|^2$ and the quantum mechanical probability current $j = -\frac{i}{2}(f^* \operatorname{grad} f - f \operatorname{grad} f^*)$. Now assume that f is nowhere zero and write $f = \exp(R + iS)$, where R and S are real-valued; then

$$\rho = e^{2R}, \quad j = e^{2R} \operatorname{grad} S. \tag{2.9}$$

Hence we see that (2.8) may be written as

$$\frac{\partial \rho}{\partial t} = \operatorname{div}(\tfrac{1}{2} \operatorname{grad} \rho - \rho \operatorname{grad} S). \tag{2.10}$$

Comparing this equation with (2.4), we recognize it as the forward Kolmogorov equation with drift

$$b = \operatorname{grad}(\operatorname{Re} \log f + \operatorname{Im} \log f). \tag{2.11}$$

This leads to:

Proposition 0

Let V be a real-valued potential function and let f be a classical solution of the Schrödinger equation

$$i\frac{\partial f}{\partial t} = -\tfrac{1}{2}\Delta_x f + Vf. \tag{2.12}$$

Suppose that f is nowhere zero and that the corresponding drift b is a continuous function of (x,t) satisfying

$$|b(x,t)| < M(|x| + 1), \tag{2.13}$$

for some positive constant M. Then, if there exist positive constants B and C such that

$$|f(x,t)| < B \exp(C|x|^2), \tag{2.14}$$

and if the transition density $p(x,0;y,t)$ exists for the diffusion process X which satisfies

$$dX_t = b(X_t,t)dt + dB_t, \tag{2.15}$$

then

$$|f(y,t)|^2 = \int_{\mathbb{R}^d} p(x,0;y,t)|f(x,0)|^2 dx. \tag{2.16}$$

The proof is a straightforward application of the uniqueness theorem for parabolic equations (see [4]). As an application we cite the following

Example:

Consider the solution

$$f(x,t) = \exp\{-\tfrac{1}{2}(x - ae^{it})^2 - \frac{a^2}{4}(1 - e^{-2it}) - \frac{it}{2}\} \tag{2.17}$$

of the equation

$$i\frac{\partial f}{\partial t} = -\tfrac{1}{2}\frac{\partial^2 f}{\partial x^2} + \tfrac{1}{2}x^2 f. \tag{2.18}$$

Then

$$|f(x,t)|^2 = \exp\{-(x - a\cos t)^2\}. \tag{2.19}$$

The corresponding diffusion process X satisfies

$$dX_t = -(X_t - a\cos t + a\sin t)dt + dB_t, \tag{2.20}$$

and the transition density p is given explicitly by

$$p(x,0;y,t) = (2\pi t)^{-\frac{1}{2}} \exp\{-\frac{(y-x)^2}{2t} + A(t,y) - A(0,x)\} E(x,0;y,t) \tag{2.21}$$

where

$$E(x,0;y,t) = E[\exp\{t\int_0^1 F(ut,(y-x)u + t^{\frac{1}{2}}b(u))du\}]; \tag{2.22}$$

here b is the Brownian bridge with $b(0) = b(1) = 0$, and

$$A(u,x) = -\tfrac{1}{2}(x - a\cos u + a\sin u)^2, \tag{2.23}$$

$$F(u,x) = A(u,x) + x(a\cos u + a\sin u) + \tfrac{1}{2}. \tag{2.24}$$

As Nelson [5] has pointed out, not all diffusions arise in this way; those which do are the conservative diffusions. To describe them, we need some definitions: the mean forward derivative D_+ is defined by

$$D_+X_t = \lim_{h \downarrow 0} \frac{1}{h} E[X_{t+h} - X_t | X_t]. \tag{2.25}$$

From (2.15) we deduce that

$$D_+X_t = b(X_t,t) = (\operatorname{grad} R)(X_t,t) + (\operatorname{grad} S)(X_t,t). \tag{2.26}$$

The mean backward derivative D_- is defined by

$$D_-X_t = \lim_{h\downarrow 0}\frac{1}{h}E[X_t - X_{t-h}|X_t]; \tag{2.27}$$

Nelson showed that

$$D_-X_t = b(X_t,t) - \text{grad}\,(\log\rho)(X_t,t) \tag{2.28}$$

so that we have

$$D_-X_t = (\text{grad } S)(X_t,t) - (\text{grad } R)(X_t,t). \tag{2.29}$$

This leads us to define the backward drift b_* as

$$b_*(x,t) = (\text{grad } S)(x,t) - (\text{grad } R)(x,t). \tag{2.30}$$

The kinetic energy T of the diffusion process is defined as

$$T(X_t,t) = \tfrac{1}{2}\{b(X_t,t)^2 + b_*(X_t,t)^2\} = \tfrac{1}{2}\{|\text{grad } S|^2(X_t,t) + |\text{grad } R|^2(X_t,t)\}. \tag{2.31}$$

A diffusion is said to be conservative if

$$\frac{d}{dt}E[T(X_t,t) + V(X_t)] = 0. \tag{2.32}$$

It is straightforward to check that the diffusion in the above example is conservative.

We turn now to diffusions associated with stationary states; we begin with an elementary proposition:

Proposition 1

Let $|f_E|$ be a classical solution of

$$-\tfrac{1}{2}\Delta_x|f_E| + V|f_E| = E|f_E| \tag{2.33}$$

such that $|f_E|>0$, where V is a real-valued potential which is bounded below. Let $p(x,y;t) = p(x,0;y,t)$ be the transition density for the diffusion process corresponding to the stationary state $e^{-iEt}|f_E|(x)$; then

$$g_E(x,y;t) = |f_E|(y)E[\exp\{\textstyle\int_0^t (E-V(x+B_s))ds\}|x+B_t = y]|f_E|(y)^{-1}, \tag{2.34}$$

where B is a $BM(R^d)$ with $B_0=0$. That is,

$$g_E(x,y;t) = |f_E|(y)\exp\{-t(H-E)\}(x,y)|f_E|(x)^{-1}, \tag{2.35}$$

where $H = -\frac{1}{2}\Delta + V$ is the Hamiltonian operator.

The proof is a simple application of the Girsanov-Cameron-Martin formula and the Feynman-Kac formula.

Remarks: (1) The process M given by $M_t = \exp\int_0^t (E-V(x+B_s))ds$ is a martingale with respect to the filtration of the Brownian motion B.

(2) The formula in (2.34) is valid whenever the Feynman-Kac formula holds

(3) The proposition enables us to discuss the asymptotics of $g_E(x,y;t)$:

(a) The large-time asymptotics can be summarized by

$$\int_{\mathbb{R}^d} g_E(x,y;t)h(x)dx \sim c|f_E|^2(y) \text{ as } t\sim\infty,$$

where $c = \int_{\mathbb{R}^d} h(x)dx$; this is merely an ergodicity result.

(b) Let $F_E^k(x,t) = \exp(-iEt/k)|f_E^k|(x)$, where $|f_E^k|$ satisfies $-\frac{k^2}{2}\Delta|f_E^k| + V|f_E^k| = E|f_E^k|$; the asymptotics for small k can be deduced for the diffusion process associated with this stationary state. For example, assume that V has a unique minimum at x=a and satisfies some mild subsidiary conditions. Using the results of Simon [5] or Davies and Truman [7], we can then deduce that

$$\lim_{k\downarrow 0}\{-k\log g_E(x,y;t)\} = \rho(a,y) - \rho(a,x) + A(x,y;t), \text{ where}$$

$$A(x,y;t) = \inf_{c\,\in\, X_0^t}\{\tfrac{1}{2}\textstyle\int_0^t |\dot{c}|^2(s)ds - \int_0^t V(c(s))ds\},\quad X_0^t = \{c:[0,t]\to\mathbb{R}^d$$

absolutely continuous, $c(0) = x$, $c(t) = y\}$ and $\rho(x,y) = \inf A(x,y;t)$ is the Agmon metric.

(4) The proposition reminds us of the extremely useful result that, for non-zero stationary states $|f_E|$ and self-adjoint quantum mechanical Hamiltonians $H = -\frac{1}{2}\Delta + V$, the generator L of the associated diffusion satisfies

$$L = -|f_E|(H-E)|f_E|^{-1},\quad L^* = -|f_E|^{-1}(H-E)|f_E|.$$

We shall make use of this in the next section

§3. Stochastic Mechanics of the Ground State of the Hydrogen Atom

In this section, we reinstate the reduced particle mass m and Planck's constant $\hbar = h/2\pi$; thus we will be concerned with the Schrödinger equation

$$i\hbar\frac{\partial f}{\partial t} = -\frac{\hbar^2}{2m}\Delta f + Vf. \tag{3.1}$$

The associated diffusion X satisfies

$$dX_t = b(X_t,t)dt + (\frac{\hbar}{m})^{\frac{1}{2}}dB_t, \tag{3.2}$$

provided f(x,t) is nowhere zero, where b is given by (2.11). The conventions of §2 remain in force, and d=3.

We shall be interested particularly in the diffusion associated with the ground state f_E of the Hydrogen atom with nucleus of charge Ze; in Gaussian units we have $V(x) = -Ze^2/|x|$ and

$$f_E(x,t) = N \exp(-|x|/a) \exp(-iEt/\hbar), \tag{3.3}$$

where a is Bohr radius and E is the ground state energy. (In Gaussian units, we have $a = \hbar^2/me^2Z$ and $E = -\hbar^2/2ma^2$.) The ground state process X satisfies

$$dX_t = -\frac{\hbar}{ma}\frac{X_t}{|X_t|}dt + \frac{\hbar}{m}^{\frac{1}{2}} dB_t. \tag{3.4}$$

The forward and backward derivatives are used to define a mean acceleration $\frac{1}{2}(D_+D_-+D_-D_+)X$ of a diffusion process X; for the ground-state process the mean acceleration satisfies Nelson's generalization of Newton's equation:

$$\frac{m}{2}(D_+D_-+D_-D_+)X_t = -Ze^2\frac{X_t}{|X_t|^3}. \tag{3.5}$$

To see this, use the formulae (which come from (3.4) and Itô's formula)

$$D_\pm X_t = \mp\frac{\hbar}{ma}\frac{X_t}{|X_t|}, \tag{3.6}$$

$$D_\pm h(X_t) = \text{grad } h \cdot D_\pm X_t \pm \frac{\hbar}{2m}(\Delta h)(X_t), \tag{3.7}$$

for an arbitrary smooth function h. When $h(x) = x/|x|$, we have grad $h \cdot D_\pm X = 0$ and $(\Delta h)(x) = -2x/|x|^3$, so that $D_+D_-X_t = D_-D_+X_t = -\frac{\hbar^2}{m^2a}\frac{X_t}{|X_t|^3}$.

Nelson has shown that his generalization of Newton's equation is valid under very wide conditions. This leads to the suggestion that the sample paths could be thought of as the unseen trajectories of the quantum mechanical particle; we now examine the sample paths of the ground-state process in more detail. We begin with:

Proposition 2

The process $|X|$ satisfies

$$d|X_t| = \frac{\hbar}{m}\frac{1}{|X_t|} - \frac{\hbar}{ma}\,dt + \frac{\hbar}{m}^{\frac{1}{2}} db_t, \tag{3.8}$$

where b is a $BM(\mathbb{R}^1)$ and $|X_0|$ has a distribution proportional to $r^2 \exp(-2r/a)$. The process $\hat{X} = \frac{X}{|X|}$ is given by $\hat{X}_t = Z(\frac{\hbar}{m}\int_0^t \frac{ds}{|X_s|^2})$, where Z is a $BM(S^2)$, a Brownian motion on S^2, the unit sphere in $\mathbb{R}^3$, with initial distribution uniform on S^2.

Proof: Using (3.4) and Itô's formula, we get (3.8) with $db = \hat{X}\cdot dB$; by the martingale characterization of Brownian motion, b is a $BM(\mathbb{R}^1)$ since $d\langle b\rangle_t = \hat{X}_t\cdot\hat{X}_t dt = dt$. Now apply Itô's formula to $\hat{X} = \frac{X}{|X|}$; we have

$$d\hat{X} = \frac{\hbar}{m}^{\frac{1}{2}}\frac{1}{|X|}(1 - \hat{X}\hat{X}^T)dB - \frac{\hbar}{m}\frac{1}{|X|^2}\,dt. \tag{3.9}$$

Let u(t) be the inverse of $t \to \frac{\hbar}{m}\int_0^t \frac{ds}{|X_s|^2}$, and put $Z_t = \hat{X}_{u(t)}$; then, by §2.5 of McKean [ ], we have

$$dZ_t + Z_t dt = (1 - ZZ^T)dB. \tag{3.10}$$

We recognize (3.10) as Stroock's equation for $BM(S^2)$ (see the contribution by J.T. Lewis in this volume) and the result follows.

We study the radial process $|X|$ in more detail:

Proposition 3

Let $g_r(x,y;t) = P[|X_t| \in dy, |X_0| = x]$ for x,y in $(0,\infty)$. Let H_r be the radial part of the Hydrogen atom Hamiltonian;

$$H_r = -\frac{\hbar^2}{2m}\cdot\frac{1}{x^2}\frac{d}{dx}\,x^2\frac{d}{dx} - Ze^2\frac{1}{x}, \tag{3.11}$$

and let $f_0(x) = \exp(-x/a)$. Then

$$g_r(x,y;t) = f_0(y)\exp\{-t(H_r - E)/\hbar\}(x,y)f_0(x)^{-1} \tag{3.12}$$

and, for each $t>0$, we have

$$-\int_0^\infty \frac{\partial}{\partial t}\{\exp(-tE/\hbar)g_r(x,x;t)\}\,dx = \sum_{n=0}^{\infty}\frac{E_n}{\hbar}\exp(-tE_n/\hbar), \tag{3.13}$$

where E_n $(n = 0,1,\ldots)$ are the eigenvalues of H_r.

The proof is a straightforward calculation. Next we investigate first hitting times for the radial process.

§4. First Hitting Times for the Radial Process

In this section we present some results on the distribution of hitting times for the radial process associated with the ground-state of the Hydrogen atom.

roposition 4

Let S_r be a sphere of radius r, with centre at the nucleus of the ydrogen atom, and assume that the initial distribution of the radial round-state process $|X|$ is the quantum mechanical ground-state probability istribution, proportional to $x^2\exp(-2x/a)$. Let $T(c,b)$ be the first itting time of the inside surface of S_c S_b, b>c, for the ground-state rocess X; then

$$E[T(0^+,b)] = \frac{2ma^2}{\hbar}\int_0^{b/a}\{\frac{\sin hu}{u} - (1+u)e^{-u}\}^2du. \qquad (4.1)$$

roof: Let $T_x[c,b] = \inf\{t\geq 0 : |X_t| \notin (c,b)^c, X_0 = x\}$, and put $v(x)=E[T_x[c,b]]$. hen, using Dynkin's identity, as explained in Professor Pinsky's ontribution to these proceedings, v is the unique solution of the quation

$$\frac{\sigma^2}{2}v''(x) + a(x)v'(x) = -1, \qquad (4.2)$$

ith $v(c)= v(b) = 0$, where $\sigma^2=\frac{\hbar}{m}$ and a(x) is given by

$$a(x) = \frac{\hbar}{m}\frac{1}{|X_t|} - \frac{1}{a}. \qquad (4.3)$$

his gives

$$v(x) = E[T_x[c,b]] = -\int_x^b[\frac{d}{x^2}\exp(\frac{2x}{a}) + \frac{2m}{\hbar}(\frac{a}{2}+\frac{a^2}{2x}+\frac{a^3}{4x^2})]dx, \qquad (4.4)$$

ith d=d(c) determined by the condition v(c)=0. Hence

$$d(c) = -\frac{m}{\hbar}\int_c^b(a + \frac{a^2}{x} + \frac{a^3}{2x^2})dx \,/\int_c^b\frac{1}{x^2}\exp(\frac{2x}{a})dx.$$

t is not difficult to show that $E[T(b)] = E[T(0^+,b)]$, so we need to alculate $c(0^+)$. Writing

$$d(c) = \{-\frac{m}{\hbar}\int_c^b a\,dx - \frac{ma^3}{2\hbar}\int_c^b\frac{2}{ax}+\frac{1}{x^2}dx\}\,/$$
$$\int_c^b(\frac{1}{x^2}\exp(\frac{2x}{a}) - \frac{2}{ax} - \frac{1}{x^2})dx + \int_c^b(\frac{2}{ax}+\frac{1}{x^2})dx \qquad (4.5)$$

e see that $d(0^+) = -\frac{ma^3}{2\hbar}$. This is precisely the value of d required o make $v'(0^+)$ finite. Repeated integration by parts completes the proof.

It is interesting to compute the orders of magnitude of the quantities nvolved here; as $\frac{b}{a}\sim\infty$. Crudely putting $e^{2u}/u^2 \sim e^{2u}$ as $u\sim\infty$, we have

$$\bar{T}(b) = E[T(0^+,b)] \sim \frac{ma^2}{4\hbar}\exp(\frac{2b}{a}).$$

If $\bar{T}(b)$ is of the order of one year, then b is of the order of 28 Bohr radii; if $\bar{T}(b)$ is of the order of the age of the universe (10^{10} years), then b is of the order of 40 Bohr radii. Hence, on the basis of stochastic mechanics, the expected first time the electric dipole moment of the Hydrogen atom, in its ground state, exceeds 28 ae is of the order of one year. These results underline the very high accuracy required to check the predictions experimentally.

Next we determine the distribution of the first hitting time by computing its Laplace transform. We require some notation: define $\bar{v}_i(x,E)$, i=1,2, by

$$\bar{v}_1(x,E) = \frac{1}{x}e^x W_{(1+2E)^{-\frac{1}{2}},\frac{1}{2}}(2(1+2E)^{\frac{1}{2}}x), \qquad (4.6)$$

and

$$\bar{v}_2(x,E) = \frac{1}{x}e^x M_{(1+2E)^{-\frac{1}{2}},\frac{1}{2}}(2(1+2E)^{\frac{1}{2}}x), \qquad (4.7)$$

where $W_{\ell,\frac{m}{2}}$ and $M_{\ell,\frac{m}{2}}$ are the confluent hypergeometric solutions of Whittaker's differential equation:

$$v''_{\ell,\frac{m}{2}} + \{-\frac{1}{4} + \frac{\ell}{x} + \frac{(1-m^2)}{4x^2}\}v_{\ell,\frac{m}{2}} = 0, \qquad (4.8)$$

and $\bar{v}_1$ is singular at x=0 and $\bar{v}_2$ is regular at x=0

To avoid notational complications we pass to dimensionless variables, eliminating Planck's constant $\hbar$ and the reduced mass m from the equations:

Proposition 5

Let $T_x(b)$ be the first hitting time of the inside surface of the sphere S_b for the diffusion associated with the ground-state of the Hydrogen atom starting at x:

$$T_x(b) = \inf\{t\geq 0 : |X_t| \notin [b,\infty]\}. \qquad (4.9)$$

Let $\bar{v}(x,E)$ be defined by

$$\bar{v}(x,E) = r\int_0^\infty e^{-Et}P[T_x(b) > t]dt.$$

Then for x in (0,b) we have

$$\bar{v}(x,E) = 2r(1 - (1+2E)^{-\frac{1}{2}}((\int_x^b w_1(y)ydy)w_2(x) - w_1(x)\int_0^x w_2(y)ydy), \quad (4.10)$$

where

$$w_1 = 0 - \frac{\bar{v}_1(b)}{\bar{v}_2(b)}^{\frac{1}{2}} \bar{v}_1 \quad (4.11)$$

$$w_2 = \frac{\bar{v}_2(b)}{\bar{v}_1(b)}^{\frac{1}{2}} - \frac{\bar{v}_1(b)}{\bar{v}_2(b)}^{\frac{1}{2}} \bar{v}_2$$

Proof: Let d be an open arcwise connected set in $\mathbb{R}^d$ and put

$T_x(D) = \inf\{s \geq 0 : Z_x(s) \in D^c\}$, Z_x being a diffusion, starting at x, with generator L. Then it can be shown that

$$P[T_x(D) > t] = \exp(t L_D^*) 1_D(x), \quad (4.12)$$

where 1_D is the characteristic function of D, and L_D^* is the adjoint of L_D, the Dirichlet form of the operator associated with the generator L with Dirichlet boundary conditions on the boundary of D. The desired result follows by taking Laplace transforms and carrying out some rather unpleasant calculations.

Remarks:

1. Since $L = -|f_E|(H-E)|f_E|^{-1}$, the last displayed equation gives

$$P[\bar{T}(D) > t] = \int_{\mathbb{R}} e^{-t(\lambda-E)} d \| E(H_D)(\lambda)|f_E| \|^2,$$

where $E(H_D)(\lambda)$ is the spectral measure corresponding to the self-adjoint operator H_D with Dirichlet boundary conditions on the boundary of D. Using this fact, we can avoid the use of Laplace transforms.

2. The above analysis can be generalized to the excited states $f_{E'}$. We must restrict ourselves to working in a connected region S, bounded by a nodal surface N, in which $f_{E'}$ is nowhere zero. We impose Dirichlet boundary conditions on N. In the region S we study the diffusion X with drift (grad) (Re + Im) log $|f_{E'}|_S|$, having generator $L = |f_{E'}|_S|(H_D^N - E')|f_{E'}|_S|^{-1}$, where H_D^N is the self-adjoint Hamiltonian with Dirichlet boundary conditions on N. (See [8].) Note that $|f_{E'}|_S|$ is the ground-state wave-function of the Hamiltonian H_D^N with eigenvalue E'. The invariant measure for the process X is $f_{E'}|_S|^2(x)dx$. Putting

$$H_D = \lim_{\lambda \to \infty} (H_D^N + \lambda 1_{SC})$$

so that $H_D \geq E'$ in the sense of quadratic forms; in this situation we obtain

$$P[\bar{T}(D) \in (t,t+dt)] = (|f_{E'}|, (H_D - E')\exp(-t(H_D - E'))|f_{E'}|)dt,$$

where $(\cdot,\cdot)$ is the inner product in $L_2(D)$, and $\bar{T}(D)$ is the expected first hitting time of the boundary of D S. (See [1].)

References

[1] A. Truman and J.T. Lewis: Stochastic Mechanics of the Bound States of the Hydrogen Atom, in course of preparation.

[2] E.B. Davies: Quantum Stochastic Processes, Commun. Math. Phys. 15, 277-304 (1969).

[3] N. Ikeda and S. Watanabe: Stochastic Differential Equations and Diffusion Processes. Amsterdam-Oxford-New York: North Holland 1981.

[4] A. Friedman: Partial Differential Equations of Parabolic Type. Englewood Cliffs, New Jersey: Prentice Hall 1964.

[5] E. Nelson, Dynamical Theories of Brownian Motion, Princeton: Princeton University Press 1967.

[6] B. Simon: Semiclassical Analysis of Low-Lying Eigenvalues, II, Cal. Tech. Preprint 1984.

[7] I. Davies and A. Truman: Laplace Asymptotic Expansions of Conditional Wiener Integrals and Generalized Mehler Kernel Formulae for Hamiltonians on $L^2(\mathbb{R}^n)$, J. Phys. A17, 2773-2789 (1984).

[8] S. Alberverio and R. Høegh-Krohn: A Remark on the Connection Between Stochastic Mechanics and the Heat Equation, J. Math. Phys. 15, 1745-1747 (1974).